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Technical Article

Pollution of Water and Stream Sediments Associated with the Vale De Abrutiga Uranium Mine, Central Portugal

M. M. S. C. Pinto, M. M. V. G. Silva, and A. M. R. Neiva

Dept of Earth Sciences, Univ of Coimbra, Largo Marquês de Pombal, 3000-272 Coimbra, Portugal; corresponding author's e-mail: marinacabral@megamail.pt

Abstract. The Vale de Abrutiga uranium deposit, located in Central Portugal near the Aguieira dam reservoir, was surface mined. Low-grade ore and waste rock were deposited on permeable ground, close to the mine, and were not revegetated. A lake has formed in the open pit. Surface waters draining the mine site are acidic, have high conductivity, and high concentrations of U, SO42-, Zn, Fe, Mn, Ra, Cu, Th, and Pb. The groundwater and the water from the reservoir cannot be used for human consumption or irrigation. The sampled waters show higher contaminant concentrations in winter than in summer. Stream sediments have high geoaccumulation indices for U, Fe, Ag, Zn, Cr, Co, and Pb. In general, sediments bordering the dam reservoir have higher metal contents in winter than in summer.

Key words: Acid drainage; Portugal; stream sediments; uranium mineralization; water

Introduction

Water pollution problems associated with mining activities are an environmental concern (Schüring et al. 1997; Rösner 1998; Castro and Moore 2000; Gabler and Schneider 2000; Marszalek and Wasik 2000; Schemel et al. 2000; Armienta et al. 2001). In Portugal, only a few studies have been reported on environmental pollution associated with mining (Nascimento et al. 1996; Oliveira 1997; Oliveira et al. 1998; Antunes 1999; Antunes et al. 2001; Oliveira et al. 2002; Silva et al. 2003), and none deals particularly with uranium mines. Pollution associated with uranium deposits elsewhere is documented (Wolkersdorfer 1996; Porcelli et al. 1997), although these examples are not specifically related to uranium phosphate mineralization, such as is reported here.

In central Portugal, about 58 uranium deposits have been exploited and later abandoned. The Vale de Abrutiga open pit mine (Figure 1) produced about 90 t of uranium oxide (U_3O_8) between 1982 and 1989. The discarded low-grade ore and waste rock (1,400,000 t) were piled on ground that was not rendered impermeable and no effort was made to revegetate them. The mine was shut down at the beginning of 1990, after which a pit lake formed. The water that fills the pit lake comes from rainfall, groundwater inflow, and from the run off of adjacent low grade ore. The acidity of the water is due to the oxidation of sulphide minerals, mainly pyrite, associated with the uranium mineralization. This acidity promotes the dissolution and mobility of metals, resulting in high conductivity values. During the rainy season, sediments are washed out of the low grade ore and waste rock, and the pit lake overflows.

The old mine is approximately 500 m away from the reservoir of Aguieira dam. The acid water from the low-grade ore, waste rock, and pit lake flows directly to the dam reservoir. The ENU (National Uranium Enterprise), which mined the deposit, has begun to reclaim the site in an attempt to reduce contamination levels. This paper assesses the extent of pollution of surface and groundwater and stream sediments in the neighbourhood of the Vale de Abrutiga uranium mine before reclamation commenced.

Sample Locations and Analytical Methods

Drill core samples from boreholes were provided by ENU. The boreholes were drilled during prospecting and intercept the mineralized body. Rock samples from several depths (0 to 25m) were analysed using a Jeol electron-microprobe JX8600 at the Dept of Earth

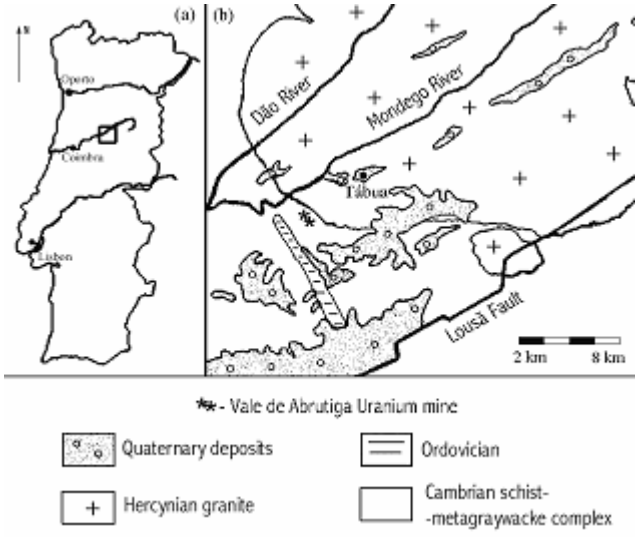

Figure 1. (a) Location of the Vale de Abrutiga uranium mine in central Portugal; (b) simplified geological map of Vale de Abrutiga area (adapted from Ponte and Pereira 1991)

Sciences, University of Bristol, U.K. and a Cameca Camebax electron microprobe, at the Geological and Mining Institute, S. Mamede de Infesta, Portugal. The precision is better than 2% and the detection limit is variable, according to the element, but is generally higher than 250 ppm. In both laboratories, 20 kV, 15 nA, and 30 seconds counting were used.

To obtain a general understanding of the distribution of contaminants in the area, water samples were collected at the surface at three points on the shore of the open pit lake (Figure 2, L1, L2, and L3), in two streams (S1 and S2), and at two points at the reservoir of the Aguieira dam (R1 and R2) in the confluence of the above-stream waters. The approximate seasonal mean surface flow rates of S1 and S2 were, respectively, 0.01 and 0.03 L/s in the dry season and 0.2 and 0.6 L/s in the wet season. Groundwater was collected from four piezometers that existed in the mined area (P1, P2, P3, and P4).

Stream sediments were collected in two streams (Figure 2, U1 and U2) that do not drain the mineralised area, in two streams that receive water from the mine drainage (D1), and from the open pit lake (D2). Shallow sediments were also collected from the border of the dam reservoir (D3 and D4), at the confluence of streams S1 and S2.

In order to study the general behaviour of the analysed chemical elements, and to do a generic physicochemical characterization in the different seasons, water and stream sediment samples were collected at each sampling point, during winters (May98, Feb99, and May99) and summer (Aug99 and Sep99). The water samples were collected after a rainless week, since rainwater would modify the chemistry and hydrodynamics of the system.

Groundwater was collected with a bailer and transferred to polyethylene bottles; surface waters were collected directly in the polyethylene bottles. The polyethylene bottles were previously washed with acid nitric solution and rinsed by demineralised water. The bottles were always completely filled, hermetically closed and kept at 4ºC. In less than 24 hours after each sampling, the water was filtered with a 0.45 µm Millipore filter, acidified with nitric acid and again kept at 4ºC. Groundwater depths were measured with an electrical probe. The approximate mean water elevations of P1, P2, P3, and P4 were, respectively, 124, 163, 172, and 165 m in the dry season, and 125, 164, 173, and 169 m in the wet season.

To assess the consistency of our seasonal results, we compared our water analyses (Table 1) to the corresponding analysis (for the same element,

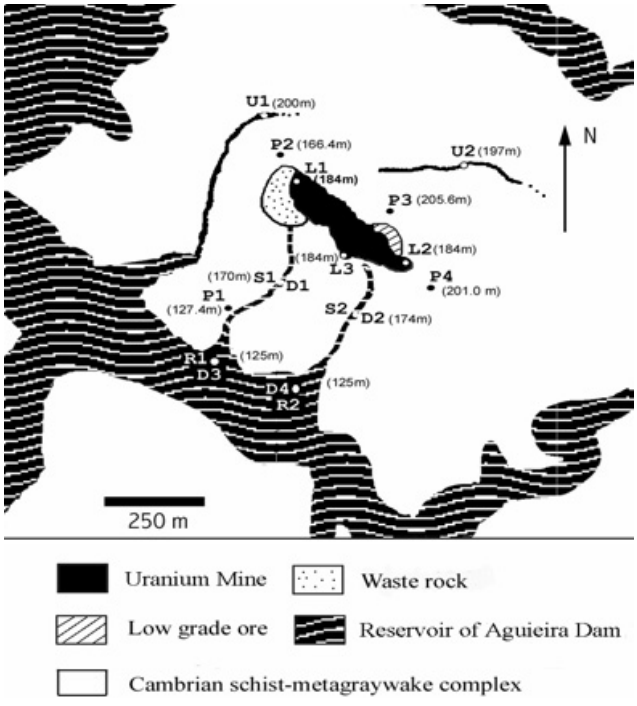

Figure 2. Sampling locations: Aguieira reservoir (R1, R2), stream waters (S1, S2), open pit lake (L1, L2, and L3), piezometers (P1, P2, P3, and P4)] upstream stream sediments: U1, U2; downstream stream sediments: D1, D2, D3, and D4] at the Vale de Abrutiga mine area. Topographic levels are shown in meters.

sampling point, and analytical method) provided by ENU (Table 2), for winter (Nov-May) and summer (Jun-Oct), from May of 1995 to March 2000.

Stream sediment samples weighing about 3 kg each were collected at 15 cm maximum depth with a small hoe into polyethylene bags, avoiding vegetation and gravel and keeping the bags open. At the laboratory, samples were left to dry in a drying oven at 40ºC. After cooling, they were disaggregated with a rubber pestle and sieved to 1 mm. After quartering, 500 g were crushed in an agate mortar to 100-mesh.

Conductivity was measured in situ with a YSI handheld conductivity meter (model 30), after calibration with a standard solution of KCl (0.00702 N); its resolution is 0.1 µScm-1 and the precision is ± 0.5%. The pH was measured in situ with a portable Crison model 507, calibrated with standard buffer solutions.

Uranium was analysed in the sampled waters by molecular absorption spectrophotometry at ENU's chemical laboratory. The detection limit is high (0.85 ppm) because the laboratory was developed for prospecting and mining. Prior to analysis, the uranium is extracted from the solution using tri-butyl-phosphate and aluminium nitrate. The formation of the yellow U-complex takes place at pH 6.5 to 9.5. The concentration of the yellow U-complex is

Table 1. Physico-chemical and chemical compositions of surface water and groundwater from the Vale de Abrutiga uranium mine region

	T	pH	C	U	SO_4^{2-}	Zn	Fe	Mn	Ra	Cu	Th	Pb
			$\mu S \cdot cm^{-1}$	$mg \cdot L^{-1}$	$mg \cdot L^{-1}$	$mg \cdot L^{-1}$	$mg \cdot L^{-1}$	$mg \cdot L^{-1}$	$Bq \cdot L^{-1}$	$mg \cdot L^{-1}$	ppb	$mg \cdot L^{-1}$
R1-s	24.1	6.29	139.7	—	—	0.21	0.12	0.49	0.53	0.01	0.01	—
R1-w	22.7	5.88	175.0	0.85	—	0.21	0.23	0.82	0.59	0.06	0.04	0.06
R2-s	24.2	5.80	117.1	—	—	0.07	0.18	0.41	0.17	0.02	0.03	—
R2-w	17.6	6.65	84.3	—	—	0.27	0.18	0.53	0.29	0.05	0.03	—
S1-s	17.2	2.53	6660.0	16.96	6576	55.00	175.70	132.90	0.31	1.14	19.60	—
S1-w	17.5	2.65	6090.0	18.66	6096	62.00	185.00	125.70	1.24	1.47	20.40	0.05
S2-s	20.5	2.69	3030.0	0.85	1872	9.10	14.70	51.30	0.34	0.02	0.64	—
S2-w	18.0	2.78	3080.0	5.90	1536	14.25	15.60	41.70	1.76	0.53	1.77	0.04
L1-s	24.3	2.25	3790.0	8.49	5280	17.80	19.80	15.10	1.07	0.72	5.12	0.05
L1-w	19.3	2.62	2906.0	8.54	3456	19.50	27.70	14.90	1.32	0.83	6.44	0.11
L2-s	23.9	2.32	3730.0	7.60	1728	17.00	19.40	15.00	0.86	0.71	4.38	0.04
L2-w	19.9	2.73	2848.0	7.60	1248	17.00	20.90	14.50	1.07	0.76	6.76	—
L3-s	13.1	2.25	3017.0	7.60	1728	17.00	19.70	14.50	0.79	0.71	4.97	0.04
L3-w	11.4	2.66	2889.0	7.65	1440	17.25	20.80	14.70	1.15	0.75	5.14	0.04
P1-s	17.4	4.80	720.0	—	240	0.09	9.20	1.30	0.52	0.02	0.03	—
P1-w	14.9	4.50	634.0	1.00	284	0.61	9.30	1.80	1.43	0.05	0.05	0.17
P2-s	18.2	5.59	399.7	—	—	0.05	0.94	0.54	0.22	0.01	0.03	—
P2-w	17.2	5.93	445.6	0.85	—	0.19	0.94	0.88	0.62	0.05	0.05	—
P3-s	18.1	5.38	174.6	—	—	0.10	0.02	0.31	0.43	0.02	0.04	—
P3-w	16.7	6.03	202.8	0.85	—	0.13	0.42	0.84	2.19	0.05	0.06	0.07
P4-s	17.3	5.66	221.0	—	—	0.03	1.70	1.20	0.61	0.02	0.05	0.05
P4-w	15.8	6.22	209.0	0.85	—	0.26	1.00	1.80	0.36	0.13	0.11	0.10

C= conductivity; — = below detection limit; s = summer, w = winter; R1 and R2 - reservoir of Aguieira dam; S1 and S2 – stream waters; L1, L2, and L3 – open pit lake; P1, P2, P3, and P4 – groundwater stations at piezometers (Figure 2)

Table 2. Physico-chemical and chemical compositions of surface water and groundwater from the Vale de Abrutiga uranium mine region, analysed by ENU

	T	pH	C	U	SO_4^{2-}	Fe	Mn	Ra
			$\mu S \cdot cm^{-1}$	$mg \cdot L^{-1}$	$mg \cdot L^{-1}$	$mg \cdot L^{-1}$	$mg \cdot L^{-1}$	$Bq \cdot L^{-1}$
S2-w	13.3	2.72	1311.0	6.21	1229	10.37	19.83	0.49
L1-s	25.9	2.39	n.d.	8.90	1404	19.60	13.10	0.55
L1-w	14.9	2.49	3353.0	9.68	1731	22.32	12.84	0.60
P1-w	14.8	5.81	718.5	3.80	288	4.77	1.35	0.30
P2-w	15.6	6.39	393.0	0.43	—	0.25	0.37	0.19
P3-w	15.5	6.13	208.5	—	—	0.05	0.21	0.30
P4-w	15.3	6.34	295.0	—	—	0.75	0.99	0.19

C= conductivity; — = below detection limit; n.d. – not determined; s = summer, w = winter; S2 – stream water; L1 – open pit lake; P1, P2, P3, and P4 – groundwater stations at piezometers (Figure 2). S2-w - Mean of May97, Apr98, and Jan99; L1-s - Mean of Jul95, Lul96, Sep96, and Jul97; L1-w - Mean of May95, Nov96, Feb97, Apr97, Nov97, Dec97, Feb98, Apr98, Nov98, Jan99, Jan00, and Mar00; and P(1 – 4)-w - Mean of Nov98, Jan99

proportional to the uranium concentration in the initial solution. The solution with the U-complex was analysed in a Philips PU 8670 UV-VIS spectro-photometer, with a wavelength of 410 nm.

We used α-spectroscopy for Ra (the detection limit is about 70 $mBq l^{-1}$), complexometry for SO_4^{2-} (detection limit = 0.01%), and atomic absorption (AA) for Fe and Mn (detection limits = 0.01 ppm). All of these analyses were done at the ENU chemical laboratory. Zn and Cu were analysed at the University of Coimbra Dept of Earth Sciences chemical laboratory, by AA, with a detection limit of 0.001 ppm and a precision of 3%. Th and Pb were analysed at the XRAL Chemical Laboratory, Canada, by ICP-MS and ICP-AES, with detection limits of 0.01 and 30 ppb, respectively (precision is between 5 and 10%). Fe, Zn, Cu, Co, and Pb in the sampled stream sediments were also analysed by ICP-AES after tri-acid digestion at XRAL Chemical Laboratory. The detection limits, in ppm, were: 100 for Fe, 0.2 for Ag, 0.5 for Zn and Cu, 1 for Co and Cr, and 2 for Pb. U and Th were determined by ICP-MS at the same laboratory with a detection limit of 0.1 ppm. The precision of the ICP-AES and ICP-MS methods is about 3 and 5%, respectively (Walsh 1997; Jarvis 1997).

Geological Setting and Mineralogy of the Deposit

The Vale de Abrutiga uranium mine is located in central Portugal, in the Mondego River basin, near the village of Tábua (Figure 1), with UTM coordinates 29TNE760656 and a topographic elevation between 250 and 300 m. The mining was by open pit. The waste rock and discarded low grade ore were deposited close to the mine in unvegetated piles with steep slopes.

In this area, a Hercynian coarse- to very coarse-grained porphyritic biotite granite, 308 ± 11 Ma, intruded a Cambrian complex of alternating phyllites and metagraywackes. The granite is peraluminous with A/CNK of 1.08-1.16 (Silva and Neiva 1999/2000). It has P_2O_5 ranging from 0.17-0.31 ppm (n=8), Th ranging from 16-59 ppm (n=8), Pb ranging from 7-24 ppm (n=8), Cr ranging from 5-18 ppm (n=8), and U ranging from 7-18 ppm (n=8) (Silva et al. 1999/2000). The granite contains magmatic uraninite $(U_{0.93}Pb_{0.05}Th_{0.04}Fe_{0.03})_{\Sigma 1.05}O_2$ (Pinto 2001), which is the main carrier and source of uranium (Basham et al. 1982). Besides uraninite, the granite contains other U-bearing minerals, like monazite, apatite, and zircon. The mineralization occurs in the weathered zone in brecciated quartz veins, which intersect the Cambrian complex close to the granite (Figure 1) and in its metamorphic contact aureole. The mineralized quartz veins fill N10ºW, 80ºE faults, which cut older, barren, NW-SE quartz veins. Weathering of minerals from the quartz veins takes place in an acidic context due to the oxidation of sulphides (pyrrhotite, arsenopyrite, pyrite, galena and sphalerite), which also occur in these veins.

The mineralization is formed by secondary uranium-phosphates: saleeite, $Mg_{0.93}Fe_{0.02}Al_{0.02}Cu_{0.01})_{\Sigma 0.98}(UO_2)_{1.99}[(PO_4)_{1.99}(SiO_4)_{0.01}]_{\Sigma 2}\bullet 10H_2O$, meta-saleeite, $Mg_{0.85}Fe_{0.01}Cu_{0.05}Na_{0.02}Ca_{0.01}Na_{0.01})_{\Sigma 0.95}(UO_2)_{1.98}(PO_4)_{2.00}\bullet 8H_2O$, and Fe-saleeite, $Mg_{0.74}Fe_{0.16}Ca_{0.01}Na_{0.01})_{\Sigma 0.92}(UO_2)_{1.96}(PO_4)_{2.00}\bullet 4H_2O$. The quartz veins also contain other uranium-bearing phases, e.g., Fe oxy-hydroxides, zircon, xenotime, monazite, anatase, muscovite, and chlorite.

Drainage from the mine enters the Aguieira dam reservoir from two streams with a length of about 500 m (Figure 2). Fe oxyhydroxide precipitation was observed in S2. During the rainy season, fine-grained sediments are washed out of the low grade ore and into to the reservoir.

Pollution of Water and Stream Sediments

Water Pollution

The conductivity, pH, and concentrations of dissolved ions are given in Table 1. The ENU analyses are presented in Table 2. Water from the pit lake and streams was strongly acid, ranging in pH from 2.3 to 2.8. Similar results were obtained by ENU for these locations. These low pH values, together with high concentrations of SO_4^{2-}, indicate pyrite oxidation. The pH of water from the reservoir ranges between 5.8 and 6.7 and is slightly higher than the pH of the groundwater, which varies from 4.5-6.2 (Table 1). The pH values of groundwater analysed by the ENU were slightly higher, ranging from 5.8 to 6.4 (Table 2).

The strongly acidic waters from the pit lake and streams have a high conductivity, ranging from 2848 to 6660 μScm^{-1}, and high concentrations of U, SO_4^{2-}, Zn, Fe, Mn, Ra, Cu, Th, and Pb (Table 1). These values are well above the maximum permitted value (MPV) for human potable water and cannot be used for irrigation, according to Portuguese law (01/08/98) and Canadian norms (Canadian Council of Ministers of the Environment 1991) (Tables 1, 3). Also, the conductivity and concentrations of U, SO_4^{2-}, Fe, Mn, and Ra obtained by ENU for these locations are well above the MPV for human potable water and irrigation (Tables 2, 3).

During summer, when the flow is low, the pH of the pit lake and stream water is slightly lower and SO_4^{2-} is higher than in winter (Table 1), which agrees with the data of Church et al. (1997) from the Animas River, Colorado. However, the concentrations of U, Zn, Fe, Ra, Cu, and Th in the pit lake and stream water are higher in winter, when the flow is high, than in summer when the flow is low. The results obtained by ENU also show higher levels of contaminants in the pit lake water in the wet season than in the dry season (Table 2).

Water from the reservoir and groundwater do not significantly differ in pH during the dry and wet season and the metal concentrations tend to be slightly higher in winter than in summer (Table 1). Higher metal concentrations during high flow are probably due to colloidal transport (Schemel et al. 2000), but the highest concentrations of U, Zn, Fe, Mn, Ra, Cu, Th, and Pb found during winter are due to interaction between larger volumes of water with the low grade ore and waste rock. This would mean that the total metal load carried by the streams is much higher during high flow (Blowes and Ptacek 1994).

The water samples from the open pit lake (L1, L2, L3) have similar compositions, but the sample from L1 has the highest contents of U, SO_4^{2-}, Zn, Fe, Ra and Pb (Table 1) because it collects the runoff coming from the waste rock. The waste rock is piled into a steep, unvegetated hill, which promotes the transport of contaminants and the erosion of materials into the open pit, increasing pollutant levels.

Water S2 flows from the open pit and has slightly lower concentrations of U, Zn, Fe, Cu, and Th and slightly higher values of pH than water from the open pit (L1, L2, and L3 in Table 1). The same results were obtained by ENU for U and Fe (Table 2). The increase in pH promotes the precipitation of Fe oxyhydroxide along the stream; the high adsorption capacity of this material for metals has long been recognized. On the other hand, water from S1 is more polluted than waters from S2 and from the open pit (Table 1), because stream S1 collects water from more sources of pollution than any other sampling point. It receives water from the open pit and from the freely drained waste rock and discarded low-grade ore, with its large-scale oxidation of sulphides.

The water from the Aguieira reservoir close to the confluence of the polluted streams (R1, R2) has normal acidity and conductivity values (Tables 1, 3). Zinc is above the maximum recommended values (MRV) for human consumption and Mn, Fe, and U (and Pb and Ra in R1) concentrations during winter are above the MPV for human consumption. This water cannot be used for agriculture because the Mn values (and U in winter) are above the MRV for irrigation. R1 receives water from the stream S1, so it is more polluted than R2, which receives water from S2.

The sampled groundwater had lower conductivity and bulk metal concentrations than the polluted surface waters (Table 1) due to the natural buffering capacity of the groundwater, which keeps the alkalinity sufficiently high to precipitate the incoming dissolved metals. However, the sampled groundwater had U, Fe, Mn, Ra, and Pb concentrations above the MPV for human consumption. In addition, the levels of Mn and U (in winter) are not suitable for irrigation (Tables 1, 3). In general, the contaminant levels in groundwater are higher in winter than in summer. Groundwater analysis by ENU also showed lower conductivity and metal concentrations than the water from the stream and pit lake; the levels of U, Fe and Mn were above the MPV for human consumption, and the U and Mn contents are not suitable for irrigation in winter (Tables 2, 3). The piezometric levels indicate that groundwater flows to the southwest, following the slope of the land surface (Figure 2). Therefore, P1 has the highest contaminant levels because it collects water from a larger number of contaminant sources (Figure 2, Table 1). Table 2 (ENU data) also shows that P1 water has lower pH and higher values of conductivity and U, SO_4^{2-}, Fe, Mn and Ra than water from the other piezometers.

Stream Sediments

According to Rose (1994), several researchers have detected seasonal effects on U anomalies in stream sediments. Therefore, sediments were collected at Vale de Abrutiga during winter and summer. Data on stream sediments and sediments from the border of the Aguieira dam are given in Table 4.

Table 3. Maximum Recommended Values (MRV) and Maximum Permitted Values (MPV) for human consumption and irrigation, according to Portuguese law (1998) and Canadian norms (1991)

	Human Consumption		**Irrigation**	
	MRV	MPV	MRV	MPV
pH	6.5-8.5	6.5-9.5	6.5-8.4	4.5-9
C (μScm^{-1})	400	500	–	–
U (mgL^{-1})	–	0.1	–	0.01
SO_4^{2-} (mgL^{-1})	25	250	575	–
Zn (mgL^{-1})	0.005	–	2	10
Fe (mgL^{-1})	0.05	0.2	5	5
Mn (mgL^{-}	0.02	0.05	0.2	10
Ra (BqL^{-1})	0.1	0.37	–	–
Cu (mgL^{-1})	0.1	–	0.2	5
Th (mgL^{-1})	–	–	–	–
Pb (mgL^{-1})	–	0.05	5	20

C= conductivity, – = no legislated limit

The fine sediments departing from the low grade ore and waste rock are transported by hydric phenomena and physical erosion, which occurs more during winter than in summer. Although the number of samples is limited, some relationships can be observed. In winter, the highest flux promotes the suspended transport of contaminants to the dam reservoir, causing sediments from D3 and D4 to have higher levels of U, Pb, Zn, Co, Cu, Th and Cr in winter (Table 4). Sediments receiving the acid drainage from the mine (D1 and D2) contain Fe oxyhydroxide precipitates, which are more abundant in summer. Consequently the adsorption of metals is strong and the sediments have the highest content of U, Fe, Pb, Zn, and Cu in summer.

There are no legislated recommended or permitted limits for contaminants in stream sediments. However, the degree of pollution by heavy metals in stream sediments has been classified using a geoaccumulation index, defined by Müller (1979): $Igeo = \log_2[Cn/(1.5 \cdot Bn)]$, where Cn = chemical element concentration (ppm) and Bn = background levels (ppm). The values of this index fall into seven classes (Table 5), where class 0 corresponds to values close to the area background. Median data from a low-density geochemical survey of Portuguese stream sediments was used to define background values for the heavy metals (Ferreira 2000; Ferreira et al. 2001).

Stream sediments upstream of the mineralized area (U1 and U2) showed no relationship between element concentrations and the season at which the samples were collected, except for Fe. Downstream of the mineralised

area, sediments were enriched in U and Fe; no major differences were found for the other elements up and downstream of the mineralised area (Table 4, Figure 3).

Sediments taken from the border of the dam reservoir (D3, D4) also have high levels of U, but Fe contents in winter are similar to background values (Table 4, Figure 3). So, the sediments are mainly contaminated with U, though Fe also contributes during the summer. All sediments collected in summer have higher Fe contents than sediments collected in the same locations in winter (Table 4, Figure 3), indicating that precipitation of Fe oxyhydroxide is lower in winter than in summer. The pH of the water is similar in both seasons, and the water is always aerobic (as indicated by the dissolved oxygen content and colour of the precipitates). In the dry season, the low discharge and evaporation promote Fe precipitation. Also, microbial activity, which is greater in the summer, may accelerate Fe precipitation. In winter, the high volumes of water promote the dilution of metals.

Sediments D1 and D2, from streams S1 and S2 that drain the mine (Figure 2), have higher Fe contents than the stream sediments upstream of the mineralised area, U1 and U2 (Table 4, Figure 3). The dissolution and precipitation of Fe (III) oxides and hydroxides in a surface environment open to air is mainly pH controlled. Although acidic conditions promote the dissolution of Fe oxides and hydroxides, the high concentrations of Fe in water draining the mine leads to its precipitation and the subsequent adsorption of U and other metals. This adsorption takes place mainly during the dry season, when the rate of Fe precipitation is the highest.

The Fe oxyhydroxides, especially in their amorphous forms, have a high capacity to retain metals, and the U affinity for Fe oxyhydroxides has been repeatedly demonstrated (Hsi and Langmuir 1985; Bruno et al. 1995; Allard et al. 1999). The capacity for retention is pH dependent but, at low pH, it is not clear how well the metals are retained (Tipping et al. 1986). The metal concentration in the solution influences U retention (Rose and Ghazi 1998). U is very mobile in surficial environments (Bell 1996), particularly in acid waters, but its high concentrations in the stream waters at Vale de Abrutiga (Table 1) promote its adsorption, which is higher in summer than in winter (Table 4) because evaporation takes place, the flux is low, and the Fe precipitation is higher. The pH of these waters is low in both seasons.

The amount of U found in sediments bordering the reservoir (D3, D4) is similar to that found in D1 and D2, from streams S1 and S2 (Table 4, Figure 2). So, I_{geo} has similar values (Figure 3), although stream waters are much more polluted in U than water from the reservoir (Table 1). This indicates that the U carried to the reservoir is fixed in its almost neutral conditions.

Table 4. Element contents of stream sediments near the Vale de Abrutiga uranium mine and background values for stream sediments

	U1-s	U1-w	U2-s	U2-w	D1-s	D1-w	D2-s	D2-w	D3-s	D3-w	D4-s	D4-w	background
U	12.8	6.1	14.5	16.4	301.	55.0	93.0	83.0	61.0	227.	27.8	83.0	5
Fe	3.15	3.02	3.61	3.54	5.46	4.07	23.9	6.37	5.75	3.45	19.0	2.70	2.45
Ag	0.6	0.4	0.5	0.6	0.5	0.4	1.3	0.8	0.6	0.5	0.9	0.4	0.1
Pb	57	18	59	65	31	28	44	40	25	29	38	38	19
Zn	137	105	155	165	803	143	196	153	161	281	130	563	74
Co	10	14	23	23	74	11	17	13	15	18	14	43	9
Cu	24.9	24.2	47.8	51.9	66.5	30.3	45.2	41.6	34.7	46.1	18.1	41.8	22
Th	10.1	8.2	12.2	11.7	9.5	8.8	3.3	9.6	9.6	10.8	5.1	7.8	5
Cr	96	86	102	107	107	105	70	106	94	103	71	83	23

Values in ppm, except for Fe which is in %. U1 and U2 – upstream; D1, D2, D3 and D4 – downstream (Fig. 2), but D1 and D2 in streams and D3 and D4 at the bottom of the reservoir of Aguieira dam; s – summer, w – winter; back. - background

The opposite behaviour was found in sediments bordering the dam reservoir (D3 and D4); they have higher U content in winter than in summer (Figure 3). In winter, the highest transport from the low grade ore occurs and the reservoir receives the largest volume of polluted water, with a pH of 2.5-2.9 (Table 1), while the pH of the reservoir is close to 6, leading to U fixation in the sediment.

The smallest I_{geo} value of U was found in stream sediments upstream of the mineralised area (U1 and U2), reaching, nevertheless, class 2 (Table 5, Figure 3). These stream sediments received contributions from

Table 5. Correspondence between I_{geo} values and I_{geo} classes according to Müller (1979)

Geoaccumulation Index (I_{geo})	I_{geo}
Igeo >5	6
$4 < I_{geo} \leq 5$	5
$3 < I_{geo} \leq 4$	4
$2 <$ Igeo ≤ 3	3
$1 <$ Igeo ≤ 2	2
$0 < I_{geo} \leq 1$	1
$I_{geo} \leq 0$	0

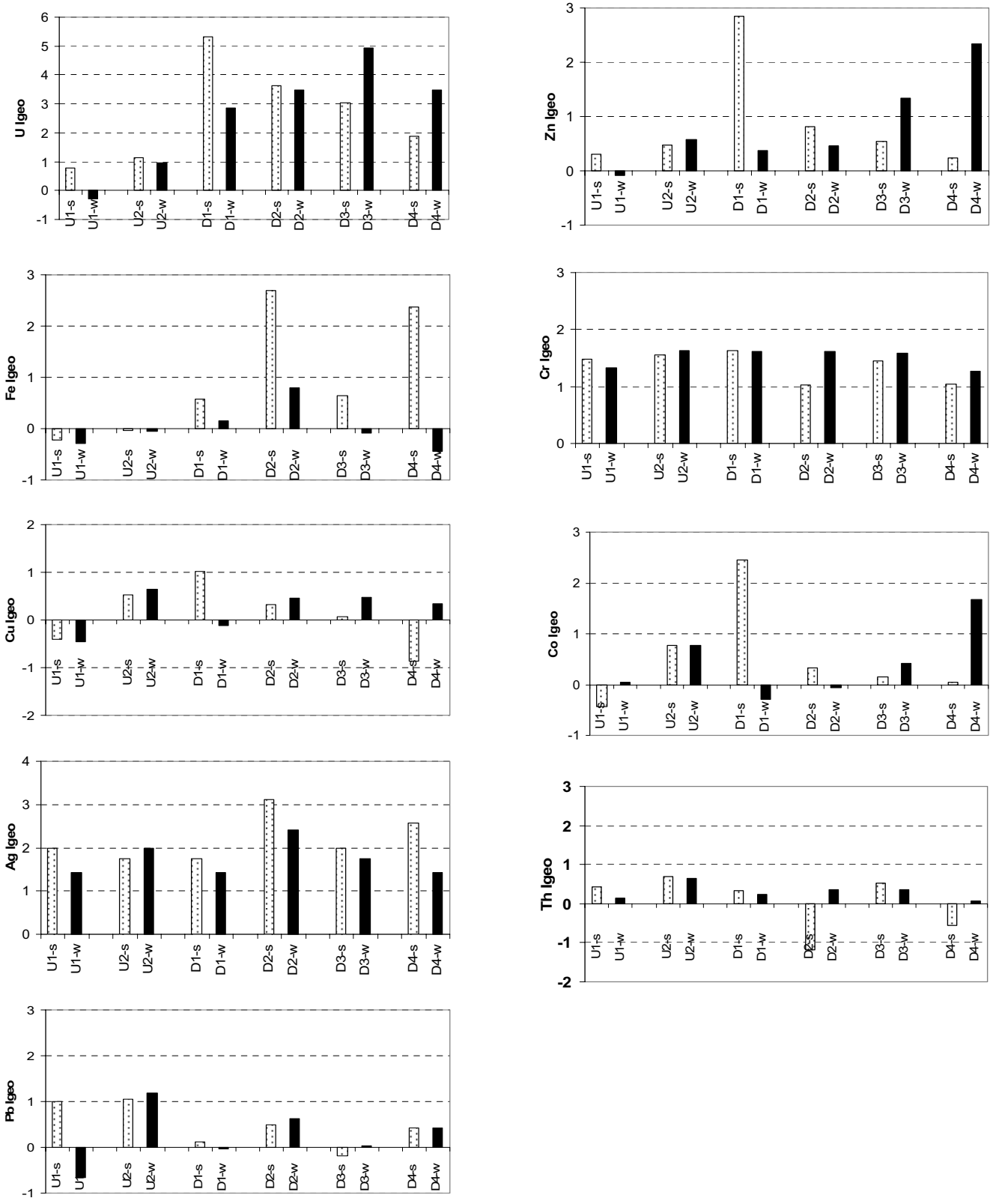

Figure 3. Column graphs of temporal and spatial variation of geoaccumulation indices of chemical elements from stream sediments near the Vale de Abrutiga uranium mine. Symbols: ⬚ - Summer (s), ■ - Winter (w); U1, U2, D1, D2, D3 and D4 - Sampling points for stream sediments (Figure 2).

the uraninite in the granite and from small mineralised veins that occur in the area. The Ag and Fe contents in stream sediments D1 and D2 are higher in summer than in winter (Table 4, Figure 3), which suggests that Ag precipitation and sorption are controlled by precipitated Fe oxides and hydroxides.

The highest I_{geo} class for Ag is 4, in D2 (Table 5), where the highest I_{geo} for Fe also occurs (Figure 3). The mineralized quartz veins contain galena and the high I_{geo} may result from the weathering of this mineral.

Pb has the highest I_{geo} in stream sediments upstream of the mineralised area (U1, U2), reaching class 2 in U2 (Figure 3). This results from the weathering of the granite, which has 7-24 ppm Pb. The mobility of Pb is generally very low in the surface environment and is controlled by pH. In streams S1 and S2, the pH ranges from 2.5 to 2.9 (Table 1), which inhibits Pb precipitation and sorption and explains why stream sediments D1 and D2 are impoverished in Pb. Upstream, the pH is neutral, promoting Pb precipitation and sorption.

Zn I_{geo} reaches class 3 (Figure 3). The highest Zn levels occur downstream from the mineralization and are likely due to sphalerite associated with the uranium mineralization in the quartz veins. Sediments bordering the reservoir (D3 and D4) are richer in Zn in winter than in summer; sediments D1 and D2 have the highest Zn contents in summer, similar to U and Fe (Table 4).

Co is frequently associated with U mineralization (Reimman and Caritat 1998), and there seems to be a correlation between U and Co downstream from the mineralization. In stream sediments D1 and D2, the Co, like the U, is higher in summer than in winter; in stream sediments D3 and D4, Co, like U, is higher in winter than in the dry season. Co reaches class 3 in D1 stream sediments in summer, when U levels reach class 6. Cu reaches class 2 Igeo in D1 stream sediments, in summer.

The Th content of the stream sediments was similar at all sampling points and no major differences were found during summer or winter. Th has low mobility (Reimann and Caritat 1998) and its consistency may be related to the nearby granite, which is rich in Th-bearing minerals like monazite (with 9% ThO_2), zircon, and apatite, or could result from the eolic transport from the accumulated low grade ore and waste rock. The I_{geo} of Th never exceed class 1 (Figure 3), indicating that this metal is retained by sediments.

Cr, like Th, has a very low mobility (Reimann and Caritat 1998) and the Cr levels are similar downstream and upstream from the mineralization, and are similar in winter and summer too. The Cr I_{geo} values are always class 2 (Figure 3), suggesting that Cr is retained by the sediments. Cr levels may be associated with the weathering of mica, which occurs in both the quartz veins and the biotite granite.

Generally, in winter, the reservoir border sediments (D3, D4) have higher levels of metals than in summer due to high discharge and physical transport.

Conclusions

The Hercynian biotite granite contains uraninite, zircon, and monazite, which were the probable sources of uranium. The uranium mine was an open pit, which overflowed after mining ceased. The water that drains from the pit lake, low grade ore, and waste rock reaches the Aguieira dam reservoir and the contacting groundwater. The water from the pit lake and drainage are heavily polluted, with low pH, high conductivities, and high metal contents, while the water from the dam reservoir has a pH close to 6, lower conductivities, and lower metal content due to dilution.

The sampled waters from the pit lake and drainage have very high values of U, Zn, Fe, Ra, Mn, Cu, SO_4^{2-}, Th, and Pb. The ionic content of these waters was higher in the studied winters than in summer because of the higher volume of acid drainage and greater erosion of materials from the waste rock and low-grade ore.

The water from the reservoir, close to the confluence of the contaminated streams, has elevated concentrations of U, Mn, Fe, Ra, and Pb, especially during the wet seasons, when discharge volumes of polluted water are high. Their concentrations are above the MPV for human consumption. They also should not be used for irrigation because their Mn (and U content in R1) is above the MPV for irrigation.

The conductivities and bulk metal concentrations measured in the groundwater samples indicate that the groundwater is less polluted than surface waters. The groundwater has concentrations of U, Fe, Mn, Ra, and Pb that are above the MPV for human consumption and values of Mn (and U in winter) above the MRV for irrigation. The metal content increases in groundwater with the increase in pollution sources, and our results suggest that the pollution is higher in winter than in summer because there is much more infiltration of polluted water.

Stream sediments have high geoaccumulation indices for U, Pb, Fe, Zn, Ag, Co, and Cr. The highest index is for U, which reaches class 6 in D1.

Sediments in streams draining the mineralised area have a higher geoaccumulation index for U and Fe than in streams that do not drain it, reflecting U sorption on Fe oxyhydroxides. The Fe content in stream sediments is highest in summer due to higher rates of Fe oxyhydroxide precipitation. In the dry season, the low

discharge, low metal dilution, the evaporation effect, and the higher bacteria activity promote Fe precipitation.

The U content of sediments bordering the reservoir is of the same magnitude as that found in the stream sediments that discharge there. The levels of most of the metals analysed were highest in winter, when the volume of polluted water was also the highest, and the metals precipitate in the almost neutral conditions of the reservoir.

Pb has the highest I_{geo} in stream sediments upstream of the mineralised area, probably due to the granite, which is rich in Pb. The occurrence of Ag, Zn and Cr in the sediments may be due to the weathering of minerals from the quartz veins.

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